UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING METALLIC FILMS OR FLAKES.

No. 865,688. Specification of Letters Patent. Patented Sept. 10, 1907.

Application filed January 19, 1907. Serial No. 353,061.

To all whom it may concern:

Be it known that I, THOMAS ALVA EDISON, a citizen of the United States, residing at Llewellyn Park, Orange, county of Essex, and State of New Jersey, have invented certain new and useful Improvements in Processes of Making Metallic Films or Flakes, of which the following is a description.

My invention relates to an improved process for making metallic films or flakes, and particularly flakes of cobalt or nickel, or of cobalt and nickel combined. In an application for Letters Patent of the United States, filed January 18th, 1907, Serial No. 353,022, I describe a process for this purpose, consisting generally in plating upon a suitable cathode alternating layers of copper and the desired metal or metallic combination, after which the composite sheet so secured is stripped from the cathode and cut up into small bodies of the desired size. Finally, the sub-divided composite bodies so secured are subjected to a suitable solution in which copper is soluble, such as cyanid of potassium, so as to free the desired films or flakes. With the process of said application, in order to facilitate the removal of the composite sheet from the cathode, I describe the application thereto of a very thin film of graphite, on which the first deposit of copper is plated.

My present process is designed as an improvement on the process disclosed in said application, and particularly in certain refinements, by reason of which the operation can be performed with greater certainty, a larger number of alternating layers can be deposited on the cathode, and the quality of the resulting films, especially as to their coherence and smoothness, will be improved. In the first place, I find that when a preliminary application of graphite is made to the cathode, no matter how carefully it may be applied, it is relatively rough and uneven, compared with the excessive thinness of the desired films, and the resulting films are therefore more or less rough and are likely to be somewhat porous. To secure the best results in storage battery work, I have found that the films which are added to the active material should be very smooth and coherent. With my present process, I provide for the ready stripping of the composite sheet from the cathode by applying the first deposit of copper in a peculiar way, so that this deposit exists in the form of so-called "cement copper" which, although perfectly smooth, is capable of being readily rubbed off of a cathode, and hence will permit the ready detachment of the composite sheet. In the next place, I find that if the composite sheet is cut up into very small composite bodies before the films are separated, as disclosed in said application, the effect of the cutting device is to compress the edges of the films, so as to make effective separation difficult even when the copper has been completely dissolved. Therefore, with my present process, I effect the dissolution of the copper after the composite sheet has been cut up into long narrow strips, but before the films have been reduced to their ultimate size, and I effect the dissolution of the copper in such a way as to materially facilitate the operation, at the same time facilitating the separation of the desired films.

My improved process is not only capable of effective use in the manufacture of films of cobalt and cobalt-nickel, but it can also be effectively carried on in connection with the manufacture of films of nickel, and in fact, when nickel films are made, I am enabled to make use of a solvent for the copper, which is cheaper and somewhat more effective than the use of cyanid of potassium in the manufacture of cobalt films. The improved process is of value in the manufacture of nickel films, because I have discovered as the result of many thousand experiments with my improved storage battery, that a considerable proportion of nickel films may be added to the cobalt films without noticeably affecting the contact conditions, and since nickel is much less expensive than cobalt, the use of an appreciable percentage of nickel films is important commercially.

In carrying my improved process into effect for the manufacture of cobalt films, I proceed as follows: The cathode is preferably a copper cylinder, having a polished nickel-plated surface. The cathod is first immersed in a suitable cobalt plating bath, preferably a concentrated solution of cobalt chlorid with cobalt anodes and while the cathode is rotating, an exceedingly thin film or blush of cobalt, say—.0001 of an inch, or less in thickness, is plated on the cathode. The cathode is now washed and is then immersed, preferably without being rotated, in a solution of copper sulfate, causing the cobalt to go into the solution and the copper to be deposited as "cement copper" in a granular, but slightly adhesive, form. Preferably, the immersion is continued only long enough to result in the covering of the cobalt film with a perfect layer of "cement copper", so as to leave a part of the cobalt film still intact. This permits the subsequent films to more perfectly retain their position on the cathode and enables a very large number of films to be deposited. If all the cobalt were dissolved in the copper sulfate bath, there would be danger of the subsequent films becoming detached during the plating, since they are deposited under a condition of tension. Instead of first depositing on the cathode a thin blush of cobalt, any other metal might be used in connection with which substantially the same reactions take place, for instance, iron, but this is not so desirable as cobalt, since the films will be liable to contamination by the iron, which would be objectionable in battery work.

Great care should be taken in keeping the acidity of the copper sulfate bath in the neighborhood of two percent by volume of free sulfuric acid. A substantial decrease in acidity would result in the deposit of a film of "cement copper", that would be totally lacking in adhesive properties, while, on the other hand, a substantial increase in acidity would make the deposit too tenacious and difficult to remove. I now introduce the cathode in a copper plating bath, using preferably a copper sulfate solution with copper anodes, and I plate a film of copper on the chemically deposited film of "cement copper." The electrodeposited film is preferably somewhat thicker than the subsequent copper films, preferably between .003 and .0035 inch, in order to secure a firm support or basis for the subsequent films. During this deposit, the cathode is preferably rotated. The cathode is now washed and then is introduced into the cobalt bath, preferably employing as stated, a concentrated solution of cobalt chlorid. In this bath, a film of cobalt of the desired thickness is deposited on the previously deposited copper film. In practice I make use of cobalt films of about .0002 inch in thickness, but obviously they may be of any thickness desired. Good results are secured with a cathode about twelve inches in diameter when the latter is rotated at from sixty to one-hundred revolutions per minute in the cobalt bath. The cathode is again washed, care being preferably taken to preserve the wash water, from which the cobalt can be precipitated by suitable reagents and a second film of copper is electrolytically deposited thereon as before. Preferably, this copper film, as well as the succeeding copper films, are made just thick enough to insure complete separation of the cobalt layers and permit the ready access of the solution, for which purpose a thickness of about .0001 inch will be sufficient. The operations described are repeated, alternating layers of copper and cobalt being deposited on the cathode until a composite sheet of the desired thickness is secured. This sheet is then cut longitudinally of the cathode, care being taken not to injure the nickel-plated surface thereof, and the sheet is then cut up into long strips, say, ten inches or more in length and about one-sixteenth of an inch in width. The resulting long filaments are now placed in a suitable open-work receptacle, for instance, a wicker basket, and introduced in a solution in which copper will be dissolved without affecting the cobalt. The solution used is preferably a thirty to forty per cent solution of cyanid of potash. In this bath, the containing vessel or basket is moved up and down, either by hand or suitable mechanism, until the copper is all dissolved, and the cobalt films are freed. I find that by thus agitating the composite strips in the bath, the time required to dissolve the copper is only about half that necessary if the films are allowed to remain quiescent, while the circulation of the liquid through the metallic mass serves to separate the cobalt films from one another. After the copper has been completely dissolved, the cobalt films are then washed and dried, preferably in a centrifuge until all traces of the cyanid are removed. The films are then annealed in hydrogen, care being taken not to have the temperature high enough to weld or "freeze" the films, after which they are cut up into small pieces in any suitable machine.

In making films of cobalt and nickel, I proceed substantially as above indicated, except, of course, that the plating bath should consist of a mixture of a suitable salt of the two metals, such as chlorid of cobalt and chlorid of nickel, and that anodes of the two metals should be used, the current being so regulated as to secure the desired relative deposit.

In the manufacture of nickel films, the operation is the same as in the manufacture of cobalt films, after the first deposit of "cement copper" has been secured. I prefer, however, in the manufacture of nickel films, instead of employing a solution of cyanid of potash to dissolve the copper, to make use of an ammoniacal copper sulfate solution, since the latter is considerably cheaper than the cyanid. The preferred proportions of this solution are eighty percent ammonium hydrate or aqua-ammonia, 5 per cent copper sulfate crystals, 5 per cent ammonium chlorid or sal-ammoniac, and 10 per cent water. In this solution the copper is readily soluble, while the nickel is not affected to the least extent. Such solution, however, is not adapted for use in the manufacture of cobalt films, since cobalt is slightly attacked thereby.

Having now described my invention, what I claim as new and desire to secure by Letters Patent is as follows:

1. The process of electroplating, which consists in chemically depositing a metal on a suitable cathode, in electroplating a metal on the deposit so formed, and in mechanically removing the said deposits from the cathode, substantially as set forth.

2. The process of electroplating, which consists in chemically depositing a metal on a suitable cathode, in electrolytically depositing the same metal on the deposit so formed, and in mechanically removing the said deposits from the cathode, substantially as set forth.

3. The process of electroplating, which consists in electroplating a thin metallic film on a suitable cathode, in chemically converting said film into a deposit of another metal, and in electroplating a metal on the chemically deposited film so formed, substantially as set forth.

4. The process of electroplating, which consists in electrolytically depositing a metallic film on a suitable cathode, in immersing the cathode with its deposit in a solution of a metallic salt, capable of reduction by the electrolytically deposited metal, whereby the latter will be dissolved and replaced by metal chemically deposited from said solution, and in finally electroplating upon the chemical deposit so secured, substantially as set forth.

5. The process of electroplating, which consists in electroplating on a suitable cathode a film of a metal capable of reducing copper from a solution thereof, then in immersing the cathode with its deposit in a solution of copper, whereby the electrodeposited metal will be dissolved and replaced by a chemical deposit of copper, and finally in electroplating upon the chemically deposited film of copper, substantially as set forth.

6. The process of electroplating, which consists in electroplating on a suitable cathode a film of a metal capable of reducing copper from the sulfate thereof, then in immersing the cathode with its deposited metal in a solution of sulfate of copper, whereby the electrodeposited metal will be dissolved and replaced by a film of chemically deposited copper, and finally, in electroplating upon the copper deposit so secured, substantially as set forth.

7. The process of electroplating, which consists in depositing a film of cobalt on a suitable cathode, then in immersing the cathode with the deposited film thereon, in a copper solution, whereby the cobalt will be dissolved and replaced by a chemical deposit of metallic copper, and finally in electroplating upon the chemically deposited copper film, substantially as set forth.

8. The process of electroplating, which consists in electroplating a film of cobalt on a suitable cathode, then in

immersing the cathode with its deposited film in a solution of sulfate of copper, whereby the cobalt will be dissolved and replaced by a chemical deposit of metallic copper, and finally, in electroplating on the chemically deposited copper film, substantially as and for the purposes set forth.

9. In a process for making metallic films, the preliminary application to a suitable cathode, of a chemically deposited film of metallic copper, as and for the purposes set forth.

10. In a process for making metallic films, the preliminary application to a cathode, of an extremely thin film of cement copper, substantially as and for the purposes set forth.

11. A process for making metallic films, comprising the application to a cathode of a chemically deposited film of metallic copper, then in applying a further film of metallic copper thereon, then in electrolytically depositing upon the latter film a film of the desired metal, then in removing the composite sheet from the cathode, and in then dissolving the metallic copper, substantially as and for the purposes set forth.

12. The process for making films of metallic cobalt or nickel, which consists in first chemically depositing on a suitable cathode a film of metallic copper, in then electrolytically depositing a copper film thereon, in then depositing on the latter film a film of nickel or cobalt or both, in then stripping the composite sheet from the cathode and in finally dissolving the copper in a solution in which the cobalt or nickel is insoluble, substantially as and for the purposes set forth.

13. The process of making films of metallic cobalt, or nickel, which consists in first depositing on a suitable cathode a film of cement copper, then in electroplating a copper film thereon, then in electroplating on the latter film a film of cobalt or nickel, or both, then in removing the composite sheet, and in finally dissolving the copper in a solution in which the nickel or cobalt is insoluble, substantially as and for the purposes set forth.

14. The process of making films of metallic cobalt or nickel, which consists in depositing on a suitable cathode alternating layers of copper and cobalt or nickel, or both, in removing the composite sheet so secured, in cutting the same into long strips or filaments, and finally subjecting the filaments to a solution in which the copper is soluble and the cobalt or nickel is insoluble, substantially as and for the purposes set forth.

15. The process of making films of metallic cobalt or nickel, which consists in depositing on a suitable cathode alternating layers of copper and cobalt or nickel, or both, in removing the composite sheet so secured, in cutting the same into long strips or filaments, in subjecting the filaments to a solution in which copper is soluble and the cobalt or nickel is insoluble, in then drying the resulting filamentary films, and in finally reducing the same to pieces of the desired size, substantially as and for the purposes set forth.

16. The process of making films of metallic cobalt or nickel, which consists in depositing on a suitable cathode alternating layers of copper and cobalt or nickel, or both, in removing the composite sheet so secured, in cutting the same into long strips or films, in subjecting the films to a solution in which the copper is soluble and the cobalt or nickel is insoluble, in drying the resulting filamentary films, in annealing the same, and in finally cutting them into pieces of the desired size, substantially as and for the purposes set forth.

17. The process of making films of metallic cobalt or nickel, which consists in depositing on a suitable cathode, alternating layers of copper and cobalt or nickel, or both, in removing the composite sheet, in cutting the sheet into long films or strips, and in finally agitating the films or strips within a solution in which the copper is soluble and the cobalt or nickel is insoluble, substantially as and for the purposes set forth.

This specification signed and witnessed this 11th day of January 1907.

THOS. A. EDISON.

Witnesses:
FRANK L. DYER,
FRANK D. LEWIS.

Correction in Letters Patent No. 865,688.

It is hereby certified that in Letters Patent No. 865,688, granted September 10, 1907, upon the application of Thomas A. Edison, of Llewellyn Park, Orange, New Jersey, for an improvement in "Processes of Making Metallic Films or Flakes," an error appears in the printed specification requiring correction, as follows: In line 12, page 1, the serial number "353,022," should read *353,002;* and that the said Letters Patent should read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of October, A. D., 1907.

[SEAL.]

EDWARD B. MOORE,

Commissioner of Patents.